

Active Sites for Coal Hydrogenation

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INTRODUCTION

The development of new catalyst systems and the understanding of reaction mechanisms are of utmost importance in the development of processes for converting coal to liquid and/or gaseous products. Mills (1) has recently reviewed some new catalytic concepts for the hydrogenation of coal. Among the effective catalysts are certain molten metal halides such as ZnCl_2 and $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$. In amounts comparable to the reactant they show hydrocracking activity for coal and polynuclear hydrocarbons (2). Although many workers have reported the use of molten salts as hydrocracking catalysts, little work has been done on the mechanism of the reactions. It is well known that these metal halides are Lewis acid type catalysts and have fairly good catalytic activity for most Friedel-Crafts reactions. Zielke et al (2) suggested that the active catalyst for the hydrocracking of polynuclear hydrocarbons may be the acid produced by the interaction of zinc chloride with water. On the other hand, when molten halides are used for coal hydrogenation, it has been suggested that they are easily decomposed in feedstocks which contain sufficient sulfur and are not the true catalysts. They are generally supposed to be partially converted to other forms such as the sulfide or oxide during the hydrocracking reaction (3).

In a previous report (4), we presented some unusual results on the dehydrogenation of 2-pentanol over several molten halide catalysts impregnated on coal. The halides, which were first heat-treated up to 400°C in a flow of N_2 , gave a high selectivity for the conversion of 2-pentanol to 2-pentanone due to the dehydrogenation reaction. It was concluded that the acidity of the halides in the solid form was very low after the heat-treatment. Thus, the role of Lewis acidity in catalysis by metal halides appears to be still open to controversy, especially when the halides are impregnated on coal.

The object of this work is to obtain a basic understanding of the catalytic behavior of molten metal halides before and after their impregnation on coal. This would give us a means of elucidating the catalytic action of the halides in the coal hydrogenation reaction.

EXPERIMENTAL

Reagent grade ZnCl_2 , $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used without purification. The halides were impregnated on Hiawatha, Utah coal (45% V.M., d.a.f. basis) from aqueous solution. In some cases, activated charcoal (AC) was used as a catalyst support for impregnation. Pretreatment was carried out overnight in a N_2 stream.

The total acidity was determined by back titration of n-butyl amine with hydrochloric acid. Basicity was also determined by back titration of benzoic acid with sodium hydroxide.

The conversion reaction of 2-pentanol was carried out continuously over fixed-bed catalysts under atmospheric pressure. The product was sampled periodically using a dry ice-methanol trap, and analyzed on a 5-ft Carbowax 20M gas chromatographic column with a flame ionization detector. The selectivity to 2-pentanone was determined as the moles of 2-pentanone produced per mole of 2-pentanol re-

acted, multiplied by 100.

Hydrogen adsorption measurements were made on one gram samples with a standard BET system. Hydrogen was introduced into the system at the initial pressure of 180-505 torr and the decrease in the pressure was recorded as a function of time.

The surface area was determined from carbon dioxide adsorption at 298°K. The Dubinin-Polanyi equation was used to calculate surface areas as described by Marsh and Sigmieniewska (5). The molecular area of carbon dioxide at 298°K was taken as 25.3 Å² (6). Nitrogen adsorption at -195°C was also carried out to obtain micro-pore surface areas.

RESULTS AND DISCUSSION

The effect of heat treatment on acidity and basicity is shown in Table I.

Table I. Surface Acidity and Basicity

Sample	Preheating temp., °C	Acidity mmol/g	Basicity mmol/g
23.1% ZnCl ₂ /coal	130	0.73	0
"	200	0.40	0
"	300	0.07	0
"	400	0.05	0
23.1% SnCl ₂ /coal	400	0.08	0

The acidity of ZnCl₂ on coal substantially decreased with the increase of preheating temperature from 130 to 400°C. The amount of basic sites was zero in all cases, irrespective of pretreatment. The acidity is nearly completely lost by pretreatment at the 400°C. Since the metal halides melt below some pretreatment temperatures, significant portions of the salt may have vaporized in the N₂ stream.

The loss of acidity on pretreatment is supported by the dehydrogenation/dehydration reaction of 2-pentanol. It is well known that relatively weak acids catalyze the dehydration of some alcohols. Accordingly, if almost all of the halides are left unchanged as acidic catalysts during the preheating process, the main products with this reaction would be olefins from dehydration rather than ketones from dehydrogenation. Table II shows the results of the activity of various molten metal halides supported on activated charcoal and coal. Activated charcoal was selected as a support because its surface acidity is too weak to catalyze the reaction under the experimental conditions. The three zinc halides and tin chloride showed conversions of 84.0 - 95.7% when supported on activated charcoal. The selectivity to 2-pentanone by dehydrogenation was about 30 to 49% for these samples. On the other hand, when the halides were impregnated on coal, they showed much higher selectivity to ketones. For FeCl₃, both conversion and selectivity were very low. As is generally expected, ZnO which is believed to be a good catalyst for hydrogenation reactions, gave 100% selectivity with a low conversion, while NiSO₄ a strong acid, showed zero selectivity to ketone.

The results of the 2-pentanol conversion reaction together with those of the acidic and basic properties indicate that there is an interaction of the molten halides with the coal, resulting in the formation of a new effective sites for the

Table II. Catalytic Conversion of 2-Pentanol

Catalyst	Pretreatment temp., °C	Reaction temp., °C	Total conv. mol %	Selectivity to 2-pentanone mol %
ZnCl ₂ on AC	404	404	95.7	31.2
ZnBr ₂ on AC	404	404	85.2	35.3
ZnI ₂ on AC	410	410	84.0	48.7
SnCl ₂ on AC	300	300	84.5	30.2
ZnCl ₂ on coal	455	405	61.9	73.5
SnCl ₂ on coal	393	387	78.2	70.4
FeCl ₃ on coal	395	395	47.8	0
ZnCl ₂ on SiO ₂	466	369	99.0	0
NiSO ₄	404	301	99.0	0
SiO ₂	404	302	19.7	0
AC	355	307	0	0
coal	404	406	5	0

dehydrogenation of the alcohol. Among the most active molten halides are ZnCl₂ and SnCl₂, which have been reported to have a strong activity for the hydrogenation of coal at short reaction times (7). Ferric chloride is a less active catalyst for hydrogenation and shows no selectivity to ketone. This indicates that the hydrogenation activity is not always dependent upon the Lewis acidity of the catalyst as proposed by Zielke et al (2). Ferric chloride is a much stronger Lewis acid than ZnCl₂ and tin chloride (8). It retains more of its acidic properties when impregnated on coal and heated, but is less effective as a hydrogenation catalyst. The possibility of basic sites being important must be rejected based on results shown in Table I.

Adsorption of H₂ on ZnCl₂, SnCl₂ and FeCl₃ impregnated on coal was measured at 200 to 415°C. Figure 1 shows typical results for hydrogen adsorption at 415°C and 505 torr. Although the slow adsorption process was detectable for several days with all samples, rapid initial adsorption was observed only with active hydrogenation catalysts. In some cases, the volume of hydrogen adsorbed amounts to 10-15 ml/g after 5 min. Original coal and FeCl₃ impregnated coal did not show any rapid adsorption under the experimental conditions. This may be important from the view point of active sites for hydrogenation. It was attempted to separate experimentally the fast and slow adsorption, as was done by Dent and Kokes (9). This work indicated that almost all of the chemisorbed hydrogen was not easily removed by degassing. The fast and slow chemisorption with the ZnCl₂ impregnated sample could not be separated. Hydrogen adsorption was markedly affected by pretreatment at 300-400°C.

It has been widely recognized that the determination of the surface areas of various coals is not straightforward. Recently, Marsh and Siemieniowska (5) proposed the use of Dubinin-Polanyi equation to calculate surface areas. The surface areas of various kinds of coals can be calculated using the equation from CO₂ adsorption data at 298°K in a conventional vacuum apparatus (6). Figure 2 shows some typical Dubinin-Polanyi plots for CO₂ adsorption at 298°K on several molten halides impregnated on coal. Excellent linear plots were obtained in all cases. Surface area results are summarized in Table III. When original coal, without any impregnation, was heat-treated in a stream of N₂ at 200° to 400°C, the surface area substantially increased to 415.8 m²/g. Once ZnCl₂ was impregnated on the coal, the surface area increased sharply with the heat temperature. Similar increases in

Table III. Surface Areas of Coal and Halide-impregnated Coals

Sample	Pretreatment temp., °C	Surface area, m ² /g	
		CO ₂ adsorption at 22°C	N ₂ adsorption at -195°C
Coal	200	170.6	1.3
	300	195.2	
	400	415.8	25.5
	1,000	109.2	25.5
ZnCl ₂ on coal (23.1%)	200	108.4	
	300	332.9	77.4
	400	581.3	432.1
SnCl ₂ on coal (23.1%)	400	557.1	317.1
FeCl ₃ on coal (23.1%)	400	471.6	206.5
ZnCl ₂ on AC	400		487.4
AC			711.5

surface area were observed with SnCl₂, but they were relatively smaller for FeCl₃. This trend of increases in surface area is in good agreement with measurements of N₂ adsorption at -195°C. This results shows that the heating of coal on which active halide hydrogenation catalysts are impregnated to 400°C, yields a much higher micropore surface area of ~ 580 m²/g. Micropores which are inaccessible for low-temperature adsorption in coals become assessible for impregnated coals. Less active FeCl₃ does not give such a sharp increase in surface area.

The nature of the active sites is as yet uncertain. A surface compound formed between the metal halide and the coal during heat treatment is thought to be responsible for the experimental observations. Lewis acidity may be important in forming this compound but is not the only requirement and does not play a role once the compound is formed. The hydrogen chemisorption properties indicate that these sites are also important in coal hydrogenation.

REFERENCES

- 1) Mills, G. A., Ind. Eng. Chem., 61, 6 (1969).
- 2) Zielke, C. W., Struck, R. T., Evans, J. M., Costanza, C. P., and Gorin, E., Ind. Eng. Chem., Process Des. Develop., 5, 151, 158 (1966).
- 3) Weller, S., "Catalysis", P. H. Emmett, ed., Chap. 7, Reinhold, New York, 1956.
- 4) Matsuura, K., Bodily, D. M., and Wiser, W. H., Preprints Fuel Chem. Div., Am. Chem. Soc., 18, No. 3, 227 (1973).
- 5) Marsh, M., and Siemieniowska, T., Fuel, 44, 355 (1965).
- 6) Walker, P. L., Jr. and Patel, R. L., Fuel, 49, 91 (1970).
- 7) Wood, R. E., and Hill, G. R., Preprints Fuel Chem. Div., Am. Chem. Soc., 17, No. 1, 28 (1972).

- 8) Cook, C., Can. J. Chem., 41, 522 (1963).
- 9) Dent, A. L., and Kokes, R. J., J. Phys. Chem., 73, 3772 (1969).

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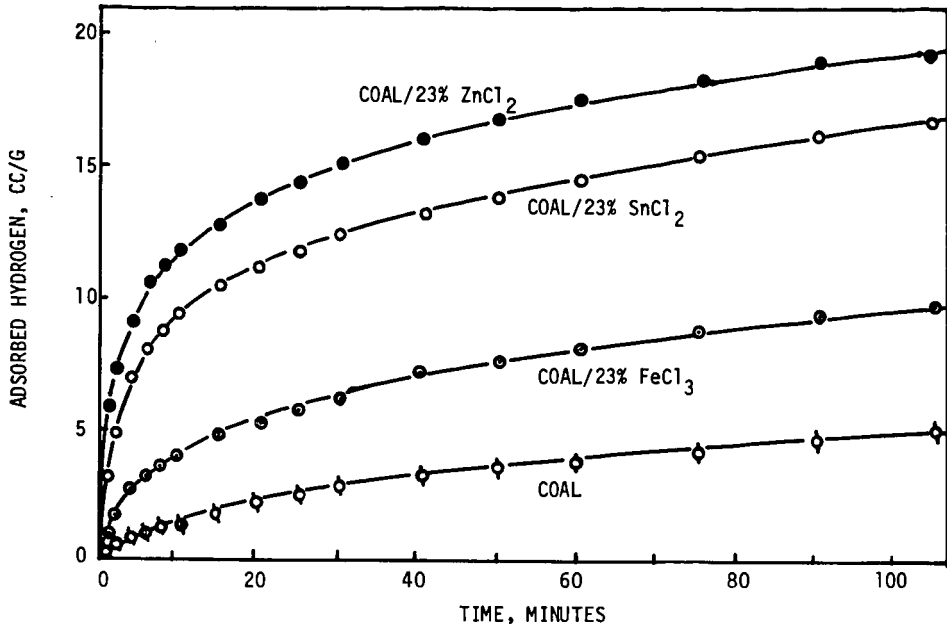
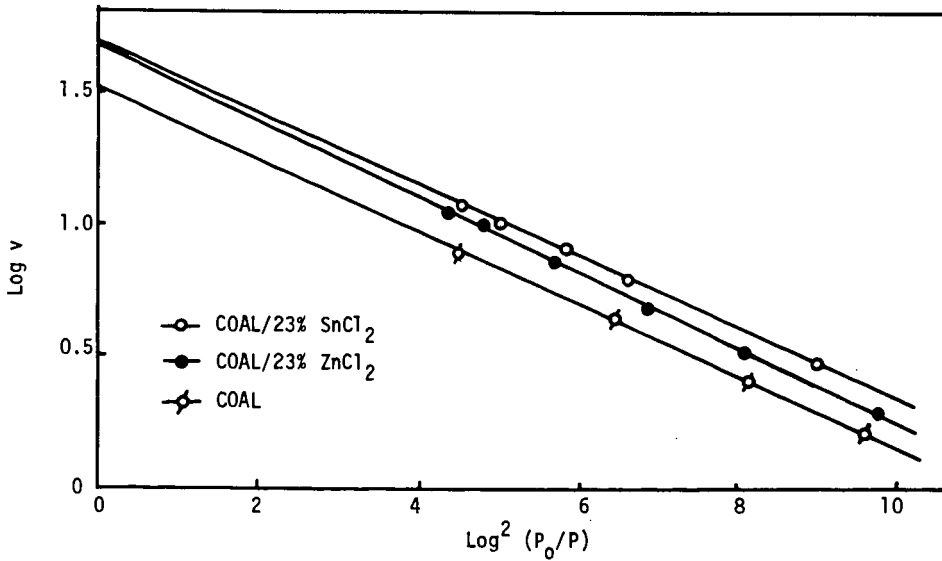


FIGURE 1. HYDROGEN ADSORPTION AT 415°C AND 505 TORR

FIGURE 2. DUBININ-POLANYI PLOTS FOR CO₂ ADSORPTION AT 298°K